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Source Resolution of Polycyclic Aromatic Hydrocarbons in the Los Angeles Atmosphere Application of a Chemical Species Balance Method with First Order Chemical Decay

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Application of a Chemical Species Balance Method with First Order Chemical Decay

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16. ABSTRACT

The chemical mass balance method which was originally developed for source resolution of chemical elements was extended in this study to chemically reactive compounds in atmospheric aerosols. The basic theoretical equation was reformulated to incorporate atmospheric decay factors for reactive species. The method was tested with selected polycyclic aromatic hydrocarbons (PAH) using source emission data and atmospheric concentrations reported in the literature. Absolute atmospheric concentrations of coronene, benzo(a)pyrene, benzo(e)pyrene, benzo(ghi)pyrene, and anthanthrene measured at 13 sites in the Los Angeles basin were apportioned between automobile and refinery emission sources.

Refinery emission patterns of PAH in the Los Angeles basin were computed from an analysis of auto emissions data and ambient data from a refinery area. Rates of atmospheric degradation of the PAH were calculated from an analysis of auto emission and ambient air data. Literature reports on major emissions of PAH from combustion sources were reviewed and evaluated.

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TECHNICAL REVIEW

This research report was accepted as a master's thesis and thus has been technically reviewed by academic peers.

Abstract

The chemical element balance method has been extended to chemically reactive components of the atmospheric aerosol. The data used for source emissions and ambient concentrations were taken from the literature. Contributions of automobile and refinery emissions to selected airborne polycyclic aromatic hydrocarbons (PAH) concentrations were determined for 13 sites in the Los Angeles basin over the period 1970-75. Automobile emissions were predominant except near a region with a large concentration of refineries. The average deviations of the calculated PAH concentrations, obtained by adding the contributions from the separate sources, from the measured concentrations were within -11% to 7%.

The data on automobile emissions were averaged over one hundred cars registered since October 1, 1971, and representative of the German automobile fleet. They were assumed to hold for the Los Angeles fleet. The source resolution could be improved by performing the same type of analysis on the Los Angeles fleet.

New data on refinery emissions and rates of atmospheric degradation of benzo(a)pyene, anthanthrene, benzo(ghi)perylene and benzofluoranthenes were obtained as a result of the analysis. Benzo(a)-pyrene and anthanthrene were found to be the most reactive species. An average residence time for aerosol particles in Los Angeles, as well as lead to PAH ratios from automobile emissions, are also reported.

The literature on PAH emissions from major combustion sources was reviewed. Agreement and discrepancies among investigators were evaluated.

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LIST OF ABBREVIATIONS

A/F	air to fuel ratio
Amu	atomic mass unit
ANT	anthracene
ANTH	anthanthrene
APCD	Air Pollution Control District
AQMD	Air Quality Management District
BaA	benzo(a)anthracene
BaP	benzo(a)pyrene
BbF	benzo(b)fluoranthene
BeP	benzo(e)pyrene
BkF	benzo(k)fluoranthene
BFL	benzofluoranthenes = benzo(b)fluoranthene + benzo(j)fluoranthene + benzo(k)fluoranthene
BghiP	benzo(ghi)perylene
CO	carbon monoxide
COR	coronene
CSTR	continuous stirred tank reactor
EM	engine modification
FLT	fluoranthene
HC	hydrocarbons
INP	indeno(1,2,3-cd)pyrene
NO_x	nitrogen oxides
PAH	polycyclic aromatic hydrocarbons
PER	perylene

PFR	plug flow reactor
PHT	phenanthrene
PYR	pyrene
TSP	total suspended particulates
FID	flame ionization detector
GC	gas chromatography
MS	mass spectrometry

I. INTRODUCTION

I.1 Air Pollution Modeling

Relating source emissions to air quality can provide a rational solution to the problem of source apportionment. Two methods of assessment have been developed separately in the past (NAS, 1980): Dispersion models and receptor models. Such predictive techniques can be used to control exposures of populations to airborne pollutants. They may also be used to foresee the impact of new technologies or shifts in technologies such as coal or wood gasification and dieselization of the automobile fleet. Thus, these methods are of considerable importance in air quality management.

Dispersion models are mathematical expressions which simulate the transport and dispersion of emissions in the atmosphere. The input variables include emission and meteorological data, initial and boundary conditions (Turner, 1979). The output gives an estimate of concentrations of pollutants over an area for various periods of time. Accuracy of these models, evaluated by computing the deviations between estimated and measured ambient concentrations, is generally controlled by the emission and meteorological data uncertainties.

Receptor models are based on empirical relationships between some known source characteristics and ambient concentrations measured at the sampling sites. Factor analysis and chemical element balances have shown to be the most powerful approaches.

Factor analysis has been recently reviewed by Gordon (1980b) and Hopke (1980). The objective of the technique is to determine the common factors (sources of emissions) which best account for the deviations in atmospheric measurements. For example, Hopke et al. (1976), using a set of 18 elements taken in 90 samples from the Boston area, showed that six common factors were responsible for 77.5% of the total variance in the system. They are sea salt, oil, auto emissions, soil (mixed with coal), refuse incineration and a sixth factor which could not be associated with a particular source.

Unlike factor analysis, the chemical element balance method assumes *a priori* that certain classes of sources are responsible for ambient concentrations of elements measured at the receptor. Furthermore, it is assumed that each source under consideration emits a characteristic and conservative set of elements (Friedlander, 1973). The method was first applied by Miller et al. (1972) to determine the contributions of sea salt, soil, automobile emissions and oil fly ash to the Pasadena aerosol. Contributions were traced by means of a mass balance on the aerosol, weighted by the mass fraction of elements present in the sources at the point of emission. Friedlander (1973) further developed the method and extended it to an overdetermined problem using a least-squares fit weighted by errors in the airborne measurements. This approach has been recently refined introducing errors in the source compositions as well as in atmospheric measurements (Watson, 1979; Dunker, 1979).

The chemical element balance method has been applied to several parts of the United States. Gatz (1975) estimated the contributions

of soil, automobile emissions, fuel oil burning, cement manufacturing, iron and steel manufacturing and coal burning at various locations of the Chicago area. Kowalczyck et al. (1978) performed a similar analysis of the Washington, D.C. aerosol. Assuming soil, marine, coal, oil, refuse and motor vehicles to be responsible for the aerosol, they were able to account for about 80% of the total suspended particulates (TSP). Dzubay (1980) in his study of the St. Louis aerosol, distinguished between the fine and the coarse fraction. Assuming that seven sources were responsible for the aerosol burden, he was able to account for 78% of the fine fraction and 96% of the coarse fraction.

A major weakness of the chemical element method is its difficulty to account for non-stable compounds. For example, secondary materials, such as sulfates and nitrates, which can be included in factor analysis must be handled separately in chemical element balances (Friedlander, 1973; Gartrell and Friedlander, 1975). As shown in this work, the methodology can be extended to a reactive part of ambient aerosols, assuming it follows first order decay laws. Polycyclic aromatic hydrocarbons (PAH) which account for a small mass fraction of urban aerosols ($\sim$0.1 mg/g of TSP) are of special interest (Dong et al., 1976; Gordon, 1976 for example). As shown later, to account for chemical decay it is necessary to develop hybrid models incorporating some elements of receptor and dispersion modeling.

I.2 Properties of PAH

PAH are by-products of the combustion of carbonaceous matter and are believed to be formed by a free radical mechanism (Crittenden and Long, 1978). They are emitted as vapors and because of their high melting and boiling points, are subsequently adsorbed onto the particulate phase and primarily soot (NAS, 1972).

Several studies on the size-distribution of PAH in urban air have shown that most of their mass is associated with smaller particles (<3 μm) and are consequently in the respirable range (Albagli et al., 1974; Katz and Chan, 1980 for example).

In the United States, the total emission rate of benzo(a)-pyrene (BaP), the most studied PAH because of its notable carcinogenicity, was estimated to approach 1300 tons/year in the early seventies (Suess, 1976). Refuse and open burning, heating and power generation and coke production were estimated to account for almost 98% of the total emissions while vehicles were believed to be responsible for less than 2%. It is evident that depending on the sampling site, these figures can vary significantly. In particular, automobile emissions are likely to dominate the overall spectrum of emissions in large cities.

Due to the recent development of high resolution analytical techniques, great improvements in the accuracy of PAH measurements have been made. It has been shown that filter losses can alter significantly the accuracy of measurements. Pupp et al. (1974) calculated the equilibrium vapor concentrations of pyrene, benzo-(a)anthracene (BaA), BaP, Benzo(e)pyrene (BeP), benzo(ghi)perylene

(BghiP), and coronene (COR). They concluded that equilibrium vapor concentrations can be considered as a measure of the collection losses upper limits. The equilibrium vapor concentration of BaA (228 amu) is almost 2 $\mu g/m^3$ at 25°C which is approximately three orders of magnitude greater than the measured atmospheric BaA concentrations. As molecular weights increase, the corresponding equilibrium vapor concentrations decrease. The equilibrium vapor concentrations of BaP (252 amu) and coronene (300 amu) at 25°C are respectively less than 0.1 $\mu g/m^3$ and 0.1 ng/m^3 indicating that, in the case of BaP, collection losses from atmospheric samples can be important. De Wiest and Rondia (1976) measured the particulate and gas phase BaP of the Liège aerosol. The reported gas phase BaP concentrations were always less than 15% of the total BaP concentrations at temperatures not exceeding 25°C, but reached 44% at 41°C. Miguel and Friedlander (1978) found no measurable BaP in the gas phase in their measurements of the Pasadena aerosol from October 1976 to March 1977.

Based on these results, atmospheric data will be analyzed for the most commonly reported PAH whose molecular weights are greater or equal to 252 amu.

II. THEORY

II.1 Chemical Element Balance Method

The chemical element balance method applied to species i can be considered to represent the equation of the center of mass of species i:

$$\rho_i = \sum_{j=1}^{p} c_{ij} m_j \qquad \text{(II-1)}$$

where ρ_i is the mass concentration of species i measured at the receptor site; c_{ij} is the mass fraction of element i present in the source m_j at the point of emission. The source contribution, $c_{ij} m_j$, is the mass concentration of element i from source m_j at the point of measurement. It is assumed that species i is conservative. If a source is missing in equation (II-1), the contribution of the others will be overestimated.

Sources are classified into classes such as automobiles, power plants and so on. Thus, aside from errors in the measurements, we induce statistical errors in the determination of the c_{ij}'s. These errors can be minimized by introducing more equations (elements) than unknowns (sources). The overdetermined system can be solved by the least-squares fitting technique (Friedlander, 1973). Suppose we measure n elements which are known to be emitted by p sources. Equation (II-1) can be rewritten with a matrix notation as follows:

$$[P] = [C][M]$$

where [P] is a n x 1 matrix whose generic term on the ith row is

ρ_i; [C] is a n x p matrix whose generic term on the ith row and jth column is c_{ij}; [M] is a p x 1 matrix whose generic term on the ith row is m_j. In order to proceed with the least-squares fitting, the following assumptions are made:

1. The errors affecting the measurement of the ρ_i's are normally distributed and uncorrelated.
2. The measured values of the source concentrations are exact.
3. The set of measurements of ρ_i's is the most probable set (maximum likelihood principle).

If the two first conditions are met, the probability, P, of observing a set of values between $\rho_1,\ldots\rho_n$ and $\rho_1+d\rho_1,\ldots\rho_n+d\rho_n$ is (Young, 1962):

$$P = \frac{1}{\sigma_{\rho_1}\ldots\sigma_{\rho_n}(\sqrt{2\pi})^n} \exp\left\{-\frac{1}{2}\sum_{i=1}^{n}\frac{\left(\rho_i - \sum_{j=1}^{p} c_{ij}m_j\right)^2}{\sigma_{\rho_1}^{\ 2}}\right\} d\rho_1\ldots d\rho_n \qquad \text{(II-2)}$$

where $\sum_{j=1}^{p} c_{ij}m_j$ represents the exact value of ρ_i obtained in the absence of error in the measurements; σ_{ρ_i} is the standard deviation in the measurement of ρ_i, i=1...n.

Assuming the measured set of values of ρ_i's represent the most probable set, it is necessary to maximize equation (II-2). In other words we have to choose the values of the m_j's which minimize the argument of the exponential function in (II-2):

$$X = \sum_{i=1}^{n}\frac{\left(\rho_i - \sum_{j=1}^{p} c_{ij}m_j\right)^2}{\sigma_{\rho_i}^{\ 2}}$$

Setting the derivative of X with respect to each m_j equal to zero

yields the result (the derivation is shown in Appendix A):

$$[D][M] = [T] \qquad \text{(II-3)}$$

where

[D] is a p x p matrix whose generic element on the jth row and mth column is:

$$d_{jm} = \sum_{i=1}^{n} \frac{c_{ij}c_{im}}{\sigma_{\rho_i}^2}$$

[M] is a p x 1 matrix whose generic term on the jth row is m_j

[T] is a p x 1 matrix whose generic term on the jth row is:

$$t_j = \sum_{i=1}^{n} \frac{c_{ij}\rho_i}{\sigma_{\rho_i}^2}$$

The source contributions can be found by solving equation (II-3). If the errors in the measurements of the ρ_i's are not known it can be assumed that they belong to the same infinite parent distribution, that is:

$$\sigma_{\rho_i} = \sigma \qquad i=1...n$$

In this case, the value of σ need not be precise since it can be eliminated from equation (II-3).

This method has been extended by Watson (1979) to cases where the uncertainties in the source concentrations are known. Assuming that these uncertainties are normally distributed and uncorrelated, especially to uncertainties in the ρ_i's, an analysis similar

to the one discussed above can be performed. However, it will not be included in the present treatment since uncertainties in refinery emissions were not known. (see section IV.2).

II.2 Extension of the Chemical Element Balance Method to Reactive Species

Mass fractions of species under consideration at the point of emission are not always available. Species of interest may react in the atmosphere. In these cases, the chemical element balance method must be reformulated. Equation (II-1) can be rewritten as follows:

$$\rho_i = \sum_{j=1}^{p} \alpha_{ij} x_{ij} y_{1j} \qquad \text{(II-4)}$$

where the dimensionless decay factor, α_{ij}, is the fraction of species i emitted from source j remaining in the aerosol at the receptor site and x_{ij} is the dimensionless ratio of mass of species i to the reference species 1 in the emission from source j. The source contribution, y_{1j}, is the mass concentration of reference species 1 from source j at the point of measurement.

It is convenient to choose as a reference species a non-reactive component of the aerosol, preferably in the same family or group under study.

The overdetermined system of n equations with p unknowns ($n > p$) can be solved by the same technique discussed in Section II-1.

Assuming that errors in the measurements are normally distributed and uncorrelated, that the decay factors and source composi-

tions are exact and applying the maximum likelihood principle, the solution to the least squares fitting is:

$$[Z][Y] = [Q]$$

where:

[Z] is a p x p matrix whose generic term on the jth row and mth column is

$$z_{jm} = \sum_{i=1}^{n} \frac{\alpha_{ij} x_{ij} \alpha_{im} x_{im}}{\sigma_{\rho_i}^2}$$

[Y] is a p x 1 matrix whose generic term on the jth row is y_{1j}.

[Q] is a p x 1 matrix whose generic term on the jth row is:

$$q_j = \sum_{i=1}^{n} \frac{\rho_i \alpha_{ij} x_{ij}}{\sigma_{\rho_i}^2}$$

The same conclusions noted in section II-1 can be drawn when errors in the measurements are not known.

II.3 Relationship of the Decay Factor to the Reaction Rate Coefficient

The decay factor, α_{ij}, accounts for the mass fraction of reacting species i emitted from source j and remaining in the aerosol at the receptor site. It is unity for non-reactive species. In the case of reactive species it can be obtained computing the ratio of atmospheric concentrations found at the receptor site to the corresponding concentrations measured at the point of emission (see section IV.1). As shown below, if the atmospheric reaction of species i follows first order

kinetics, the decay factor can be related to the reaction rate coefficient.

Let ρ_{ij} be the mass concentration of species i of the aerosol (or gas) emitted from source j. The rate of decay of species i of the aerosol is given by:

$$\frac{d\rho_{ij}}{dt} = -k_i \rho_{ij}$$

where k_i is the reaction rate constant for species i. Integrating from the time of release from the source (t = 0) to the time of collection at the receptor ($t = \tau$) yields to:

$$\frac{\rho_{ij}}{\rho_{ij,o}} = \exp(-k_i \tau)$$

where $\rho_{ij,o}$ is the mass concentration of species i emitted from source j and measured at the point of emission.

In general for any sample taken at the receptor site there will be a residence time distribution $g(\tau)$ such as:

$$df = g(\tau)d\tau$$

where df is the fraction of the material sampled with atmospheric residence times between τ and $\tau+d\tau$. The amount of species i emitted from source j remaining at the sampling point is obtained by integration over all residence times:

$$\bar{\rho}_{ij} = \rho_{ij,o} \int_0^\infty g(\tau)\exp(-k_i \tau)d\tau \qquad \text{(II-5)}$$

Further analysis requires the introduction of the residence time distribution $g(\tau)$. As a first approximation, the region of interest can be assumed to behave like a continuous stirred tank reactor (CSTR) or a plug flow reactor (PFR) at steady state. Therefore, we reduce the p sources to a unique source and ignore the decay factor dependency on the spatial distribution of the sources of emissions.

II.3.1 CSTR

In such reactors, upon introduction, the reaction immediately reaches uniform concentrations determined by the reactor volume and feed flow rate. The concentration of the species in the stream leaving the reactor are equal to the reactor concentrations (Carberry, 1976). The exponential residence time distribution is given by:

$$g(\tau) = \frac{1}{\theta} \exp(-\frac{\tau}{\theta})$$

where θ, the average residence time, is given by

$$\theta = \frac{V}{Q}$$

where V is the reactor volume and Q the volumetric feed rate. Substituting in equation (II-5) and integrating yields to:

$$\frac{\bar{\rho}_{ij}}{\rho_{ij,o}} = \frac{\bar{\rho}_i}{\rho_{i,o}} = \alpha_i = \frac{1}{1+k_i\theta}$$

where α_i is the decay factor specific to species i and $\rho_{i,o}$ is the mass concentration of species i measured at the point of emission.

II.3.2 PFR

In this type of reactor, all entering molecules have the same residence time which is given by the ratio of the reactor volume to the volumetric feed rate:

$$\frac{\bar{\rho}_i}{\rho_{i,o}} = \alpha_i = \exp(-k_i\theta)$$

III. SOURCE CONCENTRATIONS OF PAH

As discussed in the preceding section, source resolution through the chemical element balance method is based on the knowledge of two types of data: ambient measurements at the receptor sites (ρ_i's) and source concentration matrix (c_{ij}'s) of emissions measured at the point of emission. Furthermore, since the method cannot account for each source but instead types of sources (automobile emissions, coke production and so on), it is necessary to develop a source concentration matrix which is statistically representative of the types of sources under study. For this purpose, a literature review of PAH emissions from major combustion sources and an evaluation of agreement and discrepancies between investigators is presented in this section.

III.1 Coal Combustion

Junk and Ford (1980) reviewed the literature on organic emissions, including PAH, from coal combustion, waste incineration and coal/refuse combustion. In the case of coal combustion emissions, sources will be separated into home heating and power generation.

PAH emissions are higher when the combustion is incomplete and/or non uniform (NAS, 1972). Thus, emissions from coal-fired power plants are expected to be less than those from residential furnaces, for the same amount of fuel burned. Hangebrauck et al. (1967) have studied PAH emissions from different units depending on the unit size, its operating conditions, fuel and design parameters,

They showed that emissions from hand-fired residential furnaces were much larger than emissions from any other type of unit. This result is in agreement with the observations of Natusch (1976). Ratios of emissions with respect to coronene presented by Hangebrauck et al., were not reproducible even within the same type of unit probably because of the many variables affecting the PAH formation. Nevertheless, for all types of units, emission rates of higher molecular weights (greater or equal to 252 amu) were less important than those of lower molecular weight PAH. Similar patterns were reported by Lee et al. (1977). Recent measurements (Bennett et al., 1979) on emissions from three coal-fired power plants showed that emissions of PAH heavier than 226 amu were generally smaller than the minimum detection limit (0.1-0.2 ng/Nm^3). Natusch (1978) suggested that most of the measured PAH in the stack were still present as vapors since their mass concentrations were, in the aerosol phase, larger in the vicinity of the coal-fired power plant than in the stack itself. Concentrations measured in the plume at a distance ranging from zero to five miles away from the stack were approximately two orders of magnitude higher than concentrations reported by Bennett et al. for PAH heavier than 226 amu.

III.2 Coke Production

Particulate and gaseous phase emissions from coke ovens have been measured for their PAH content (Bjørseth et al., 1978). Samples were taken on top of the coke oven batteries in Spring and Fall 1976 before and after reconstruction of a Norwegian coke plant. A signifi-

cant mass fraction of the phenanthrene (178 amu) and anthracene (178 amu) sampled were shown to be present in the gas phase (∿8-50%). Traces of BaP and BeP (∿0-2%) were also found in the gas phase. Table 1 shows a comparison of Bjørseth's emission ratios with respect to perylene (PER), with the results of Btoddin et al. (1977) and Lao et al. (1975). Table 1 also shows some aspects of the sampling conditions used by the different investigators. The fit between Bjørseth and Broddin is good while discrepancies with the results of Lao are noted for the BeP, ANTH and BghiP perylene ratios.

III.3 Incineration

Emissions are likely to depend on the type of material burned. Hangebrauck et al. (1967) examined PAH emissions from two municipal and two commercial incinerators burning wastes from households, grocery stores and restaurants. Mass fractions of emissions were one to two orders of magnitude higher for the smaller units (commercial incinerators) than for the larger ones. Pyrene, fluoranthene and phenanthrene were predominant in all types of units. The same result was observed by Bjørseth et al. (1978) and Lao et al. (1975) in the case of coke oven emissions. However, a municipal incinerator burning an average composition by weight of 32% paper, 18% fine dust and cinder, 15% vegetable and putrescibles, 9% metal, 8% textile and wood, 7.5% glass and ceramic and 5% plastic and rubber, was shown not to emit significantly higher emission rates of fluoranthene and pyrene than other PAH reported (Davies et al., 1976).

Table 1. Comparison of PAH to perylene emission ratios from coke production.[a]

Reference	PAH/PER						
	BaP	BeP	BFL	ANTH	BghiP	COR	Sampling conditions; sampling point, type of filter used, method of extraction and analysis.
Bjørseth et al. (1978)	5.0[b]	2.9	3.6	1.3	1.4	1.5	0.3-0.5 m above the floor, on top of the coke oven batteries. Acropore filters. Soxhlet extraction. GC/MS analysis.
	4.6[c]	2.2	2.9	1.8	3.0	0.6	
Broddin et al. (1977)	10.7		-	-	3.1	-	8 m away from the top of the coke oven batteries. Anderson cascade impactor equipped with glass fiber filters. Soxhlet extraction. GC/MS analysis.
Lao et al. (1975)	3.7	0.1	3.8	0.1		1.2	No information on the sampling point. Glass fiber filters or silver membrane filters. Soxhlet extraction. GC/UV, GC/MS, GC/FID analysis.
	5.5	0.0	7.9	0.0		0.0	
	3.3	0.0	3.6	0.0		1.4	
	3.3	0.0	4.1	0.0		1.1	

[a] PAH lighter than 252 amu are not included in this table. Perylene was chosen for reference since it was reported by all investigators.

[b] Samples were taken before modification in coke plant.

[c] Samples were taken after modification.

III.4 Wood Combustion

Emissions resulting from the combustion of wood and peat in a hot water boiler were measured for their PAH composition (Alsberg and Stenberg, 1979). Peat combustion emissions were approximately one order of magnitude higher than wood combustion emissions due to a less complete and less uniform combustion. As shown in Table 2, emission ratios of selected PAH with respect to BghiP were generally found similar for both fuels. Phenanthrene, pyrene and fluoranthene were predominant while only traces of coronene were detected.

Table 2. Selected PAH to BghiP emission ratios from wood and peat combustion. Adapted from Alsberg and Stenberg (1978).[a]

Fuel \ PAH / BghiP	PHT	ANT	FLT	PYR	BaA	BaP	BeP	PER	INP
Wood[b]	55	4.2	23.5	19	3.4	1.4	2.7	0.2	0.8
Peat	45	3.7	19.4	16	4.7	0.4	2.4	0.2	1.5

[a] Data on coronene were not usable. BghiP (276 amu) was chosen for reference. BghiP is believed to be one of the least reactive PAH (see Table 5).

[b] Arithmetic mean over 3 experiments.

III.5 Open Burning

Several types of open burning have been surveyed for their PAH emissions: municipal refuse, landscape refuse, automobile components (Hangebrauck et al., 1967; Gerstle and Kemnitz, 1967), automobile tires (Hangebrauck et al., 1967). Both investigators used

the same sampling train, and emission ratios with respect to a species of reference are in excellent agreement. Pyrene and fluoranthene emissions were predominant. Emissions of anthracene and phenanthrene were surprisingly low when compared to BaP emissions. This does not seem to be the pattern for emissions from other sources.

Forest fires can become a locally important source of PAH. MacMahon and Tsoukalas (1978), simulating a pine needle fire, have reported emissions factors for PAH species from anthracene to BghiP. Coronene was not detected. The mass fractions of the 18 PAH reported depended on the type of fire (i.e. with the wind or against the wind) and on the mass concentration of fuel burned. Emission ratios with respect to a reference species were not reproducible.

III.6 Gasoline-powered Cars

Although diesel emissions per mile may be larger, of all mobile sources gasoline-powered vehicles are likely to be the predominant source of PAH emissions and to contribute a significant amount of the PAH found in urban atmospheres. Emissions depend on many variables and the following presentation will differentiate vehicle characteristic effects from fuel composition effects (NAS, 1972).

Vehicle characteristic effects. When the mixture is rich (i.e. cold start) combustion is less complete than during lean combustion and PAH emissions are expected to be higher. Williams and Swarin (1979) showed that average emission rates from seven gasoline, non-catalyst cars were more than six times higher in cold

starts. In the vicinity of the stoichiometric air to fuel ratio (A/F = 14.5) PAH emissions were shown to be constant (Begeman and Colucci, 1970; Pedersen et al., 1980). Begeman and Colucci also reported thirty times greater emissions of BaA and BaP at A/F = 10 than at 14. The BaA to BaP emission ratio varied from 3.1 to 3.7, showing a maximum at A/F = 14, when the air to fuel ratio was kept between 12 and 16. For the reasons stated above, PAH emissions vary according to the driving mode. Begeman and Colucci (1970) showed that BaP emissions were at a minimum of 3.3 µg/g of tar for a 30 mph cruise, reached 16 µg/g for a 50 mph cruise and peaked at 21.4 µg/g during acceleration. The BaA to BaP emission ratios were respectively 7, 5.4 and 3.9. Over-consumption of oil (9.1 qt/1000 miles instead of 0.26 qt/1000 miles) based on a 2000 mile run on a 1968 (EM) vehicle, was responsible for about a tenfold increase in BaP emissions while the BaA to BaP emission ratios decreased respectively from 4.5 and 5.6 to 1.6 and 0.9. In the same fashion, Begeman and Colucci (1970) showed that, for a city driving cycle, an eightfold increase in the oil consumption (200 miles/qt instead of 1600 miles/qt) induced a tenfold increase in BaP emissions and an eightfold increase in BaA emissions. Statistically, mileage did not affect the BaA and BeP to BaP emission ratios from a 1968 (EM) and a 1970 (EM) vehicle (Gross, 1974).

Fuel composition effects. Fuel lead content was shown to have no significant effect on PAH emissions (Gross, 1971; Pedersen et al., 1980). It is generally believed that an increase in the

fuel PAH content increases PAH emissions (Pedersen et al., 1980; Newhall et al., 1973; Gross, 1972) but seems not to affect significantly PAH emission profiles (emission ratios with respect to a species of reference). A fuel BaP content increase of 3 ppm caused a 32% increase in BaA emissions and an 8% increase in BaP emissions from a 1970 (EM) vehicle (Gross, 1972). Newhall et al. (1973) testing 1969, 1970 and 1972 vehicles did not show statistically significant differences in the BaA to BaP emission ratio when using a fuel with no PAH and a fuel containing 0.8 and 2.2 ppm of BaP and BaA, respectively. Similarly, at a 30 mph cruise, the BaA to BaP emission ratio varied respectively from 7.3 to 6.8, at constant BaP fuel content (1.1-1.2 ppm), when the BaA fuel content was changed from zero to 1.3 ppm (Begeman and Colucci, 1970). Newhall et al. (1973) showed that increasing the C_6-C_8 fuel aromatic content from 8% to 38.1% increased BaA and BaP emissions from 1969, 1970 and 1972 vehicles by a factor of one to 3.5 depending on the vehicle while the BaA and BaP emission ratios, within the same vehicle, were not significantly affected. However, the type of fuel aromatic fraction, at a 40 vol.% constant aromatic content, was shown to strongly influence PAH emission profiles; for example, the BaA to BghiP emission ratios were approximately four and nine for an o-xylene and a C_9+C_{10} aromatic fraction, respectively (Pedersen et al., 1980).

Grimmer and Hildebrandt (1975) investigated PAH emissions from 100 passenger cars registered since October 1, 1971, in West Germany. A detailed analysis of their data, which were those used

for automobile emission profiles in our source resolution, is presented in section IV.1.

III.7 Diesel-powered Cars

The impact of a possible dieselization of the United States passenger vehicle fleet is currently of interest. At the present time, emissions from diesel engines are unlikely to account for a significant amount of atmospheric PAH found in urban areas. A 1975 inventory of BaP emissions in the Los Angeles atmosphere (Abrott et al., 1978) pointed out that the estimated daily load from diesel engines was less than 6% of the total emissions listed. Gasoline-powered vehicles accounted for more than 84%.

BaP emission rates were found to be similar in cold starts for gasoline-noncatalyst cars and diesel cars (Williams et al., 1979). They averaged 5.1 µg/mile for seven gasoline-noncatalyst cars and 3.9 µg/mile for one 1978 diesel car. The diesel car was a 1978, 5.7 L, 8 cylinders burning a diesel fuel No. 2 containing 0.11 ppm of BaP. The noncatalyst, gasoline cars were burning an unleaded fuel containing 1.04 ppm BaP. The average hot start emission rates were higher for the 1978 diesel car than for the seven gasoline-noncatalyst cars, 1.9 µg/mile and 0.8 µg/mile, respectively.

The BaA and BaP emission rates from one diesel engine (a six cylinder Mack ENDT-675, four cycle, turbo charged engine with direct injection) burning a composite of ten commercial $N^{o}2$ diesel fuels, were determined at no load, half load and full load (Brickmeyer and

Spindt, 1978). Emission rates of BaP, averaged over five runs, varied from 8 to 25 μg/kg of fuel burned. They were minimum at half load. The BaA to BaP emission ratios were 2.7, 3.9 and 1.1 at idle, half load and full load, respectively.

Kaschani (1979) presented a gas chromatogram of PAH in diesel exhaust gas showing that pyrene, fluoranthene and phenanthrene were the predominant species. Coronene, BaP and perylene peaks were notably smaller than BeP, BghiP and chrysene peaks.

IV. SOURCE RESOLUTION ANALYSIS FOR LA PAH: RESULTS AND DISCUSSION

IV.1 Automobile Emissions--PAH Decay Factors

In the preceding section, PAH emissions and emission profiles from gasoline-powered cars were shown to depend on many variables. In order to compute a PAH emission profile representative of automobile emissions, a survey type of study was needed.

Grimmer and Hildebrandt (1975) surveyed PAH emissions from 100 passenger cars representative of the German automobile fleet (twenty most common models and five cars per model). The selection of the models chosen "was made by the percentage they held of the total number of first registrations from January to May 1972. These 20 models represent 67.07 percent of all newly registered passenger cars." All vehicles chosen were registered since October 1, 1971. They were supplied by dealers, car rentals or private owners. These cars were tested simulating a city driving mode (Europa-Test). They were submitted to a technical control before being tested. In particular, "compression, spark plugs, ignition timing and contact angles, CO and HC content during idling and tightness of the exhaust system were checked. If necessary, ignition timing and contact angles were corrected. The CO concentration, when too high, was regularly reduced to 2 to 3 vol.%, or, when too low, increased to these values." The crankcase oil was not changed and the code of fuel used was ERF/G1. No information was given on

the characteristics of the various models tested. Reproducibility of the chemical analysis was checked by analyzing 10 times the same exhaust condensate. The variation coefficients of single PAH were within 2.8 to 5.8%.

A statistical evaluation of PAH to coronene emission ratios was performed for PAH molecular weights starting from 252 amu since these emission profiles are to be compared with ambient PAH concentrations. The choice of 252 amu has been discussed in the introductory section. Our analysis included BaP, BeP, BFL, ANTH, BghiP and INP. Emission ratios with respect to coronene are shown in Table 3. The standard deviation of each PAH to coronene ratio was within 15% to 41% of the arithmetic mean of emission ratios from the 20 models tested. This result suggests that PAH emission ratios are not strongly dependent on the model tested. In support of this last statement, results were checked for consistency with atmospheric samples taken in Cincinnati (Sawicki, 1962) and Los Angeles (Gordon, 1980a) at sites which are likely to be dominated by automobile emissions (Table 3). In the analysis which follows, the arithmetic mean of emission profile calculated from the data of Grimmer and Hildebrandt was assumed typical of automobile emissions in Los Angeles over the period 1970-75. It was further assumed that the deviation between the data of Gordon (1980a) and Grimmer et al. (1975) is due to a first order decay in all species of interest. The assumption of first order decay is supported by the results of Katz et al. (1979) and Lane and Katz (1977). They performed experiments on simulated atmospheric degradation of BaP, BeP,

Table 3. PAH Pattern Comparisons

Reference	Grimmer and Hildebrandt (1975)	Gordon (1980a)	Sawicki (1962)	Sawicki (1962)	Sawicki (1962)
Sampling Point / PAH / COR	Tailpipe of cars *e*	Site 1 *a* (LA)	Tailpipe of cars	Cincinnati downtown garage) (January)	Cincinnati Auto Safety Lane (January)
BaP	0.50±0.14	0.27±0.11 *b* 0.23±0.06 *c* 0.23±0.06 *d*	0.71	1.3	0.41
BeP	0.51±0.12	0.48±0.08 0.56±0.09 0.53±0.05	0.55	0.78	0.62
BFL	0.55±0.13	0.54±0.07 *f*	--	--	--
INP	0.40±0.09	0.70±0.17 *g*	--	--	--
BghiP	1.58±0.24	1.32±0.24 1.21±0.17 1.39±0.21	3.0	2.08	2.62
ANTH	0.29±0.12	0.05±0.03 0.06±0.02 0.07±0.02	0.24	0.32	0.52

a Site 1 (see Table 9) was near a freeway junction, nearest freeway 0.12 mile, with heavy traffic and was not close to any known stationary combustion source at the time of sampling.

b,c,d Arithmetic mean within 68% of 12 samples taken on a monthly basis from 6/71 to 6/72, 12/72 to 12/73 and 2/74 to 1/75, respectively.

e Arithmetic mean within 68%.

f Samples were taken on a monthly basis from 12/72 to 12/73.

g Samples were taken on a monthly basis from 2/74 to 1/75.

BkF and BbF observing first order decay laws. Falk et al. (1956) observed a 16% degradation of coronene after a four hour irradiation under a strongly oxidizing synthetic smog (∿30 ppm oxidant). Light intensity did not seem to affect the stability of coronene (Barofsky and Baum, 1976; Falk et al., 1956). Based on these results, coronene was assumed to be a stable species in our analysis.

Computing the ratios of Gordon's to Grimmer's emission profiles with respect to coronene provided decay factors for each PAH. Indeno (1,2,3-cd) pyrene, (INP), was not included since its ratio to coronene at the receptor site was greater than the same ratio at the point of emission. This discrepancy could not be explained.

Decay factors were first calculated on a quarter basis for samples taken in downtown Los Angeles from June 1971 to June 1972, December 1972 to December 1973, and February 1974 to January 1975. Due to stronger photochemical conditions, PAH decay factors were expected to be higher during the second and third quarters of the year. Since that was not found to be the case after statistical analysis of the data, the data were randomized and solved for their arithmetic mean. A propagation of errors analysis was performed assuming uncorrelated errors (Bevington, 1969). Results showed a stronger reactivity for BaP and ANTH than for BeP, BghiP and BFL (Table 4).

An eleven hour average atmospheric residence time based on lead concentration and morning inversion height was computed (Appendix B). PAH were assumed not to react after deposition in the filter media since they were no longer exposed to solar radia-

Table 4. PAH Decay Factors[a]

PAH	Decay Factor
BaP	0.48±0.21
BeP	1.04±0.29[b]
BFL	0.98±0.26
BghiP	0.83±0.19
ANTH	0.21±0.11

[a]Arithmetic mean within 68% confidence.

[b]BeP was assumed a stable species in the source resolution analysis.

tion which probably accounts for most of their removal (NAS, 1972). This assumption is supported by the fact that Miguel and Friedlander (1978), sampling with glass fiber filters and a low pressure impactor during 72 hours from October 1976 to March 1977, and Gordon (1980a) operating with high volume samplers for a three week period from August 1974 to January 1975, have found similar BaP to coronene ratios for nearby sampling sites (0.14 to 0.22 and 0.26, respectively).

Reaction rate constants were calculated assuming that atmospheric residence times were equal to those for a continuous stirred tank reactor (CSTR) or a plug flow reactor (PFR). As expected, reactivity is greater for the CSTR model than the PFR; the difference being less marked for less reactive species such as BghiP and BFL than for more reactive species such as BaP and ANTH.

Results were compared with data reported in the literature for PAH degradation in laboratory experiments or simulated atmospheres (Table 5). The data shown are not self-consistent. For example, since PAH react readily with ozone or other oxidant (NAS, 1972), BaP reactivity is expected to increase with the oxidant content of the reactants. However, this is not the case when the results of Tebbens et al. (1971) and Falk et al. (1956) are compared with each other. Similarly, it is believed that PAH degradation is less important in the absence of irradiation. But irradiation, all other parameters being equal, did not affect significantly the reactivity of BaP and BeP while a tenfold increase in reactivity was observed in the case of BbF and BkF (Katz et al., 1979; Lane and Katz, 1977). On the other hand, Korfmacher et al. (1980) carrying out experiments on

Table 5. Comparison of rates of degradation of selected PAH.

Reference	System	Adsorbent	Reactant	Light Intensity	Rate Constants hr^{-1}
Falk et al. (1956)	Static system	Pure and unadsorbed	hν and pure air	Not given	ANTH 0.018 BaP 0.008 BghiP 0 COR 0
			hν, smog (~30 ppm oxidant)	Not given	BaP 0.41 BghiP 0.23 COR 0.10
		Soot	hν and pure air	Not given	ANTH 0.0011 BaP 0.0022 BeP 0.0015 BghiP 0
			hν, smog (~30 ppm oxidant)	Not given	ANTH 0.8 BaP 0.2 BeP 0.7 BghiP 1.1
Karatsune and Hirohata (1962)	Static system	Solution of cyclohexane	UV lamp, pure air	2.6×10^{13} quanta/s/cm^2	BaP 0.0064
Tebbens et al. (1966)	Flow reactor	Smoke from propane burning	hν, SO_2 (8-10 ppm)	Not given	BaP 0.49
			hν, SO_2 (50-80 ppm)		BaP 0.74
Tebbens et al. (1971)	Flow reactor	Soot	hν and pure air	21-30 W/m^2	BaP 1.06
				14 W/m^2	BaP 0.62
Barofsky and Baum (1976)	Carbon needle	Carbon	hν and pure air	2 W/m^2	BaP 0.041 COR 0
Lane and Katz[a] (1977)	Semi static system	Cellulose	hν and pure air	quartzline lamp, 46 cm above the samples	BaP 0.13 BbF 0.08 BkF 0.05 BeP 0.03
Katz et al.[a] (1979)			hν, pure air and 0.2 ppm O_3	(9.4×10^{13} quanta/s/cm^2)	BaP 1.19 BbF 0.17 BkF 0.18 BeP 0.13
			Dark, pure air and 0.2 ppm O_3		BaP 1.12 BbF 0.013 BkF 0.020 BeP 0.091
This work	CSTR	Atmospheric samples taken in Los Angeles (Site 1). See text for assumptions.			ANTH 0.342 BaP 0.098 BeP 0 BFL 0.002 BghiP 0.019
	PFR				ANTH 0.142 BaP 0.067 BeP 0 BFL 0.002 BghiP 0.017

[a] Rate constants shown were obtained from the corresponding PAH half-lives reported by the authors. Other rate constants were calculated assuming first order decay.

the degradation of PAH adsorbed onto the coal fly ash concluded that their reactivity was dependent on the type of adsorbent. Thus, reaction rates reported in Table 5 should be compared with caution.

IV.2 Refinery Emissions

The data used are those of Gordon and Bryan (1973) and Gordon (1980a). Again, it was assumed that site 1 (Gordon and Bryan, 1973) was dominated by automobile emissions. Site 3 (Gordon and Bryan, 1973) was near to and downwind from a concentration of petroleum refineries and chemical plants. The nearest freeway was within 1.27 miles and the traffic was moderate. Site 3 was not close to any other known stationary combustion source at the time of sampling, but it was assumed to receive contributions from refineries and automobiles.

Gordon and Bryan (1973) measured the lead concentrations at sites 1 and 3 from June 1971 to June 1972. Automobiles were assumed to account for the lead concentrations found at these sites. Thus, lead was used to trace automobile emissions at site 3 since site 1 was assumed to be totally dominated by automobile emissions. Refinery emissions were obtained by computing the difference between each PAH concentration measured on a monthly basis from June 1971 to June 1972, at site 3 (Gordon, 1980a), and the corresponding calculated PAH concentration resulting from automobile emissions at that site for the same period of time. Table 6 shows profiles of emissions with respect to BeP, from automobiles and refineries. It constitutes the source concentration matrix that was used to solve the

Table 6. Source Concentration Matrix

Source of Emissions	PAH/BeP				
	BFL	BaP	BghiP	ANTH	COR
Automobiles (Grimmer et al., 1975)	1.08±0.36	0.98±0.36	3.10±0.87	0.57±0.27	1.96±0.46
Refineries[a]	1.43	3.85	2.46	2.12	0.23[b]

[a] All PAH were corrected for their decay.

[b] Based on small coronene concentrations.

chemical species balance. BeP is believed to be a stable species (see Table 4). It was used as the reference species, instead of coronene, since coronene emissions from refineries are small and the accuracy of our result is uncertain in this case. However, the calculated coronene emissions from refineries are generally one order of magnitude smaller than other PAH emissions under consideration. And this last result is in agreement with findings of Bennett et al. (1979) who investigated PAH emissions from an oil fired power plant burning a Venezuelan residual fuel.

Lead concentrations measured at sites 1 and 3 from December 1972 to December 1973, were also reported by Gordon (1980a). An alternative approach, in order to compute the refinery emission profiles, was to average the profiles obtained from the data of June 1971 to June 1972 and December 1972 to December 1973. Results are shown in Appendix C. Emission profiles are similar to those shown in Table 6. Furthermore, when the chemical species balance is solved using the new set of data for refinery emission profiles, it yields almost identical results to those shown in Tables 7 and 8. This approach was not taken into consideration since it provided negative refinery emissions in the case of coronene.

Another type of analysis was performed by Gordon and Bryan (1973). They showed that coronene correlated well with traffic density. And assuming that automobiles were responsible for the concentration of coronene measured at sites 1 and 2 (see Table 9 for the site locations), they were able to determine the PAH concentrations, resulting from non-automobile emissions, measured at site 3.

Again, this method yielded almost identical results to those shown in Tables 7 and 8, but was not selected since it assumed that refineries did not emit coronene.

IV.3 Source Resolution

The chemical species balance was solved for 13 sites in the Los Angeles basin. It was assumed that automobiles and refineries were the *only* sources to contribute significantly to the coronene, BaP, BeP, BFL, ANTH and BghiP measured at the stations. A set of four, five or six equations, depending on how many species were measured at the different receptor sites, was solved according to the least-squares fit technique. In all cases, errors in the measurements were assumed equal since they were not known (see section II.1). Uncertainties on the elements of the source concentration matrix were ignored since they could not be determined in the case of refinery emissions. The atmospheric concentration vectors were based on data reported by Henderson et al. (1975) and Gordon (1980a). Results are shown in Tables 7 and 8 together with the atmospheric concentration vectors, Table 9 shows the locations of the sampling sites.

As shown in Table 7, refinery contributions were found to range between zero and 13% at site 1, depending on the PAH, the year or the period of year that samples were taken. In fact, there should have been *no* contributions from refineries at that site, as a result of the calculations, since one of the constraints of our analysis was to assume that site 1 received contributions from auto-

mobiles *only*. As stated previously (p. 27), average decay factors, for each PAH under study, were found by computing the ratios of Gordon's to Grimmer's emission profiles. Gordon's emission profiles were the arithmetic mean over samples taken from June 1971 to June 1972, December 1972 to December 1973, February 1974 to January 1975. They deviated from their three year mean value when computed on a quarterly or yearly basis. These deviations are responsible for the residual refinery contributions found at site 1. The results of the calculation indicate that the PAH concentrations at site 1 were indeed dominated by automobile emissions.

Site 2, near site 1, followed a similar pattern. The refinery contributions peaked at site 3 where the fractions of BaP, BFL and ANTH due to refinery emissions varied from 0.73 to 0.94. This result is in agreement with the locations of refineries (Bryan, 1974). Sites 4, 10 and 13 also received significant amounts of PAH emitted by refineries. The BaP and ANTH mass fractions due to refineries at these sites, varied from 0.15 to 0.27. Other stations, not in the vicinity of refineries, were shown to be automobile dominated. Contributions for sites 1, 2, 3 and 4 were calculated on a yearly basis and for the second and third quarters of the corresponding years. Results showed a similar pattern suggesting that home heating is not an important source of PAH, at least in Los Angeles.

Inconsistent results were sometimes found (i.e. slightly negative refinery contributions) due to errors in the source concentration matrix, decay factors and/or ambient concentration vectors. In these cases, errors in ambient concentration vectors are most

likely responsible for the inconsistencies since these were associated with the smaller concentrations. A tentative solution was performed on a monthly basis but did not yield satisfactory results. In this case, the atmospheric concentration vectors, based on a single measurement, may have generated errors in the source resolution. The method also failed to yield reasonable results when the source concentration vectors were based on the data of Gordon (1976). Specifically, significant contributions of refineries were found for regions 7 and 8 (see Table 10 for the region locations) whereas no contribution of refineries was found for regions 9, 10 and 12.

The ratios of lead to PAH from automobile emissions, computed whenever lead concentrations were available, are also shown in Tables 7 and 8. Their arithmetic means within the 68% confidence are shown in Table 11 and are in agreement with emissions profiles computed from the data of Grimmer and Hildebrandt. Table 11 also shows the average deviations of the calculated PAH concentrations from the measured concentrations at the different receptor sites. These deviations can be regarded as a measure of the accuracy of our results. They are within -11 to +7 per cent of the measured concentrations.

Table 7. Contributions of automobiles and refineries to selected airborne PAH at various locations in Los Angeles.

Station [a]	Year/ Period	PAH	Automobile Contributions ng/m^3	Lead/PAH [b] x10^{-3}	Refinery Contributions ng/m^3	Total Calculated PAH Concentrations ng/m^3	Measured Concentrations ng/m^3	% Deviation from Measurements
1	June 71	COR	4.50	--	0.02(0)	4.52	4.66	- 3
	to	BaP	1.08	--	0.16(1)	1.24	1.37	- 9
	Oct. 71	BeP	2.30	--	0.08(7)	2.39	2.29	+ 4
		BghiP	5.90	--	0.17(8)	6.08	6.08	0
		ANTH	0.28	--	0.03(9)	0.32	0.23	+39
1	June 71	COR	4.86	1.10	0.01(1)	4.87	4.87	0
	to	BaP	1.17	2.20	0.09(0)	1.26	1.36	- 7
	June 72	BeP	2.48	2.16	0.04(9)	2.53	2.38	+ 6
		BghiP	6.37	0.70	0.10(0)	6.47	6.51	- 1
		ANTH	0.30	5.79	0.02(2)	0.32	0.24	+33
1	Dec. 72	COR	4.57	0.93	0.01(2)	4.58	4.82	- 5
	to	BaP	1.10	1.87	0.09(0)	1.20	1.20	0
	Dec. 73	BeP	2.33	1.83	0.05(2)	2.38	2.55	- 7
		BghiP	5.99	0.59	0.10(6)	6.10	5.88	+ 4
		ANTH	0.28	5.23	0.02(3)	0.30	0.33	- 9
		BFL	2.46	1.70	0.07(3)	2.53	2.59	- 2
1	May 74	COR	2.52	--	0.00(6)	2.53	2.58	- 2
	to	BaP	0.60	--	0.04(9)	0.65	0.63	+ 3
	Oct. 74	BeP	1.29	--	0.02(7)	1.32	1.39	- 5
		BghiP	3.30	--	0.05(4)	3.35	3.30	+ 2
		ANTH	0.15	--	0.01(2)	0.16	0.19	-16
1	Feb. 74	COR	4.06	--	0.00(4)	4.06	3.77	+ 8
	to	BaP	0.97	--	0.03(6)	1.01	0.98	+ 3
	Jan. 75	BeP	2.07	--	0.02(0)	2.09	1.97	+ 6
		BghiP	5.32	--	0.04(0)	5.36	5.47	- 2
		ANTH	0.25	--	0.00(9)	0.26	0.27	- 4
2	June 71	COR	2.16	--	0.00(4)	2.16	2.19	- 1
	to	BaP	0.52	--	0.03(9)	0.56	0.58	- 3
	Oct. 71	BeP	1.10	--	0.02(1)	1.12	1.19	- 6
		BghiP	2.83	--	0.04(3)	2.87	2.83	+ 1
		ANTH	0.13	--	0.00(9)	0.14	0.12	+17
2	June 71	COR	2.86	0.87	0.00(0)	2.86	2.94	- 3
	to	BaP	0.69	1.38	0.00(2)	0.69	0.74	- 7
	June 72	BeP	1.46	1.35	0.00(1)	1.46	1.44	+ 1
		BghiP	3.78	0.43	0.00(2)	3.78	3.73	+ 1
		ANTH	0.17	2.37	0.00(0)	0.17	0.14	+21
3	June 71	COR	1.08	--	0.29	1.37	1.63	-16
	to	BaP	0.26	--	2.30	2.56	2.68	- 4
	Oct. 71	BeP	0.55	--	1.25	1.80	1.88	- 4
		BghiP	1.42	--	2.55	3.97	3.77	+ 5
		ANTH	0.07	--	0.55	0.62	0.56	+11

Table 7 (continued)

Station [a]	Year/ Period	PAH	Automobile Contributions ng/m^3	Lead/PAH [b] x10^{-3}	Refinery Contributions ng/m^3	Total Calculated PAH Concentrations ng/m^3	Measured Concentrations ng/m^3	% Deviation from Measurements
3[c]	June 71	COR	1.78	1.11	0.33	2.11	2.12	0
	to	BaP	0.43	2.21	2.67	3.10	3.14	- 1
	June 72	BeP	0.91	2.16	1.45	2.36	2.29	+ 3
		BghiP	2.33	0.70	2.95	5.28	5.30	0
		ANTH	0.11	5.79	0.64	0.75	0.72	+ 4
3	May 73	COR	0.49	2.47	0.25	0.74	1.01	-27
	to	BaP	0.12	4.84	2.03	2.15	2.23	- 4
	Oct. 73	BeP	0.25	4.84	1.10	1.35	1.76	-23
		BghiP	0.64	1.57	2.25	2.89	2.54	+14
		ANTH	0.03	8.64	0.49	0.52	0.46	+13
		BFL	0.26	4.48	1.54	1.80	2.20	-18
3	Dec. 72	COR	1.49	1.37	0.35	1.84	2.12	-13
	to	BaP	0.36	2.71	2.80	3.16	3.20	- 1
	Dec. 73	BeP	0.76	2.68	1.52	2.28	2.60	-12
		BghiP	1.95	0.87	3.10	5.05	4.64	+ 9
		ANTH	0.09	4.73	0.67	0.76	0.74	+ 3
		BFL	0.80	2.48	2.13	2.93	3.63	-19
4	June 71[d]	COR	0.18(0)	--	0.00(2)	0.18(2)	0.204	-11
	to	BaP	0.04(3)	--	0.01(3)	0.05(6)	0.064	-13
	Oct. 71	BeP	0.09(2)	--	0.00(7)	0.09(9)	0.104	- 5
		BghiP	0.23(6)	--	0.01(5)	0.25(1)	0.234	+ 7
		ANTH	0.01(1)	--	0.00(3)	0.01(4)	0.012	+17
4	June 71[d]	COR	0.18(8)	2.66	0.00(1)	0.18(9)	0.211	-10
	to	BaP	0.04(5)	5.32	0.01(0)	0.05(5)	0.063	-13
	June 72	BeP	0.09(6)	5.21	0.00(5)	0.10(1)	0.109	- 7
		BghiP	0.24(7)	1.68	0.01(1)	0.25(8)	0.240	+ 8
		ANTH	0.01(1)	9.55	0.00(2)	0.01(3)	0.011	+18

[a] See Table 9 for the site locations.

[b] All PAH were corrected for their decay.

[c] Deviations from measurements are due to computational error and to the fact that decay factors are based on samples taken from June 71 to June 72, December 72 to December 73 and February 74 to January 75.

[d] Except August 1971 (incomplete data).

Table 8. Contributions of automiblies and refineries to selected airborne PAH at various locations in Los Angeles.

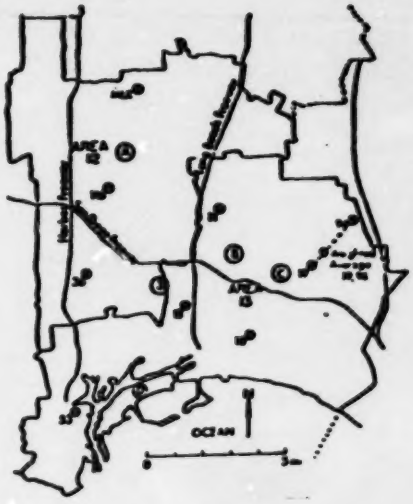
Station [a]	PAH	Automobile Contributions ng/m^3	Lead/PAH α x10^{-3}	Refinery Contributions ng/m^3	Total Calculated PAH Concentrations ng/m^3	Measured [b] Concentrations ng/m^3	% Deviation from Measurements
53	COR	0.64	1.55	-0.00(3)	0.64	0.74	-14
	BaP	0.15	3.09	-0.02(4)	0.13	0.15	-13
	BeP	0.32	3.09	-0.01(3)	0.31	0.31	0
	BghiP	0.83	0.98	-0.02(7)	0.80	0.74	+ 8
36	COR	0.97	1.14	0.00(2)	0.97	1.03	- 4
	BaP	0.24	2.27	0.01(6)	0.26	0.26	0
	BeP	0.49	2.27	0.00(9)	0.50	0.48	+ 4
	BghiP	1.28	0.72	0.02(7)	1.31	1.26	+ 4
116	COR	0.77	1.52	-0.00(3)	0.77	0.89	-13
	BaP	0.18	3.08	-0.02(4)	0.16	0.18	-11
	BeP	0.39	3.00	-0.01(3)	0.38	0.40	- 5
	BghiP	1.01	0.96	-0.02(7)	0.98	0.89	+10
MLK	COR	0.79	1.18	-0.00(0)	0.79	0.90	-12
	BaP	0.19	2.33	-0.00(2)	0.19	0.21	-10
	BeP	0.40	2.33	-0.00(1)	0.40	0.37	+ 8
	BghiP	1.05	0.74	-0.00(2)	1.05	0.98	+ 7
11	COR	1.01	1.31	0.00(1)	1.01	1.17	-14
	BaP	0.24	2.59	0.00(8)	0.25	0.29	-14
	BeP	0.51	2.59	0.00(4)	0.51	0.47	+ 9
	BghiP	1.34	0.82	0.00(9)	1.35	1.25	+ 8
94/19	COR	0.86	1.47	-0.00(1)	0.86	1.00	-14
	BaP	0.21	2.93	-0.00(4)	0.21	0.23	- 9
	BeP	0.44	2.86	-0.00(2)	0.44	0.45	- 2
	BghiP	1.14	0.92	-0.00(4)	1.14	1.04	+10
10	COR	0.70	1.70	0.00(8)	0.71	0.80	-11
	BaP	0.17	3.40	0.06(4)	0.23	0.25	- 8
	BeP	0.36	3.31	0.03(4)	0.39	0.36	+ 8
	BghiP	0.92	1.07	0.07(1)	0.99	0.94	+ 5
13	COR	0.98	1.12	0.01(1)	0.99	1.07	- 7
	BaP	0.24	2.24	0.08(8)	0.33	0.34	- 3
	BeP	0.50	2.20	0.04(8)	0.55	0.64	-14
	BghiP	1.29	0.71	0.09(7)	1.39	1.32	+ 5

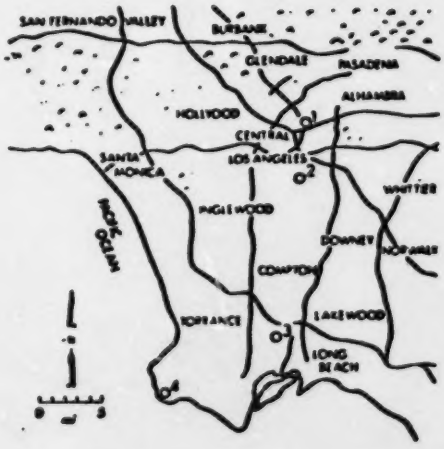
[a] All PAH were corrected for their decay.

[b] Extracted from Henderson et al. (1975). The data shown are the "fitted mean values of four weekly sample composite".

[c] See Table 2 for the site locations.

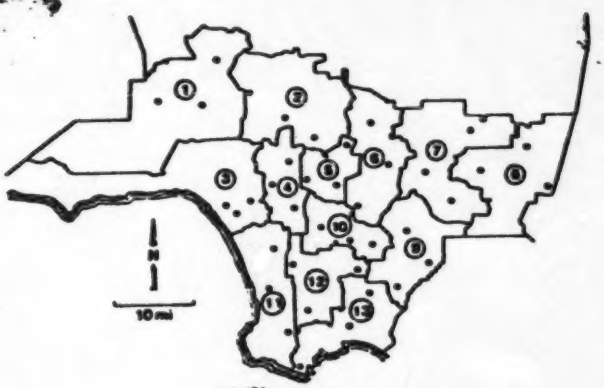
Table 9. Los Angeles Sampling Sites with Freeway Network[a]





[a]Taken from Gordon and Bryan (1973) and Henderson et al. (1975).

Table 10. Los Angeles County divided into 13 areas (excluding sparsely populated northern portion). Dots denote air sampling sites.[a]



[a]Table from Gordon (1976).

Table 11. Average lead to PAH ratios from automobile emissions and percent deviations of calculated PAH concentrations from measured concentrations.[a]

	Lead/PAH x 10^{-3}	Deviations from Measured Concentrations (in %)
COR	1.40±0.47	-9±6
BaP	2.77±0.98	-7±6
BeP	2.73±0.96	-1±8
BFL[b]	2.09	-11
BghiP	0.87±0.31	+6±4
ANTH	4.97±3.21	+7±12

[a]Arithmetic mean within 68% confidence of data shown in Tables 7 and 8. Data from Table 7 not covering an entire year were ignored. The June 71-June 72 results for sites 1 and 3 were also ignored since they were biased by our assumptions (see p. 31).

[b]Arithmetic mean of the two values shown in Table 7 for samples taken from Dec. 72 to Dec. 73 at sites 1 and 3.

V. CONCLUSIONS AND FURTHER CONSIDERATIONS

The chemical element balance method has been modified to account for reactive species assuming that they follow a first order decay process. Application of the method to airborne PAH in the Los Angeles basin has shown that automobile emissions generally predominate. Significant non-automobile contributions were found for sites near refineries. Some of the assumptions made in this work can be relaxed or eliminated as follows:

1. An analysis similar to that of Grimmer and Hildebrandt (1975) for the German automobile fleet should be performed for the Los Angeles automobile fleet. This would ensure that the values for automobile emissions used in the source concentration matrix are representative.
2. Coronene was assumed to be a non-decaying species in carrying out the source resolution. This assumption is not needed if mass fractions of species with respect to the TSP, present in the source at the point of emission, are known.
3. The dependence of the decay factors on the locations of emission sources was ignored. This allowed dramatic simplification in the decay factor calculations. However, it must be taken as a first approximation which can be upgraded by dividing the region of interest into grids to account for the non-uniform distribution of emissions. Such

a model has been previously used to estimate the spatial and temporal distribution of CO, HC and NO_x emissions within Los Angeles (Reynolds et al., 1973; Roth et al., 1974).

The limiting assumptions made in the calculation of rates of PAH degradation, aside from those stated above, were the following:

a. The eleven-hour average residence time of particles of the Los Angeles aerosol, based on morning inversion height and lead concentration, is representative of the average residence time of the polycyclic organic matter.

b. PAH do not react after deposition in the filter media.

An assumption similar to assumption a has been made in the past. Lemke et al. (1969) estimated an average residence time of one day for air in the Los Angeles basin, based on a 500 m inversion height and carbon monoxide concentration.

Assumption b has been justified previously. Errors induced by this postulate can be minimized by using polytetrafluoroethylene membrane filters thus, avoiding the catalytic action of glass and silica surfaces as pointed out by Lee et al. (1980).

This work has also summarized much of the data on PAH emissions from major combustion sources available in the literature. It was shown that data, within the same type of source (i.e. coal-fired power plants, incinerators and so on), were generally not in a good agreement. Thus, the selection of the data to be included in the source concentration matrix often seemed speculative.

In our analysis, representative automobile emission profiles, obtained from published data, have been used to deduce refinery emission profiles. A similar strategy can be applied to infer representative source concentrations from other classes of sources.

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APPENDIX A

The weighted sum of the squares of the differences between the measured and the calculated concentrations can be developed as follows:

$$X = \sum_{i=1}^{n} \left\{ \frac{\left(\rho_i - \sum_{j=1}^{p} c_{ij} m_j \right)^2}{\sigma_{\rho_i}^2} \right\}$$

$$= \sum_{i=1}^{n} \frac{\rho_i^2}{\sigma_{\rho_i}^2} - 2 \sum_{i=1}^{n} \sum_{j=1}^{p} \frac{\rho_i c_{ij} m_j}{\sigma_{\rho_i}^2}$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{p} \frac{c_{ij}^2 m_j^2}{\sigma_{\rho_i}^2} + 2 \sum_{i=1}^{n} \sum_{\substack{j=1 \\ m>j}}^{p-1} \sum_{m=1}^{p} \frac{c_{ij} c_{im} m_j m_m}{\sigma_{\rho_i}^2}$$

Differentiating X with respect to source m_j and equating the result to zero yields the solution:

$$0 = -2 \sum_{i=1}^{n} \frac{\rho_i c_{ij}}{\sigma_{\rho_i}^2} + 2 \sum_{i=1}^{n} \frac{c_{ij}^2 m_j}{\sigma_{\rho_i}^2} + 2 \sum_{i=1}^{n} \sum_{\substack{m=1 \\ m \neq j}}^{p} c_{ij} c_{im} m_m$$

$$= -2 \sum_{i=1}^{n} \frac{\rho_i c_{ij}}{\sigma_{\rho_i}^2} + 2 \sum_{i=1}^{n} \sum_{m=1}^{p} c_{ij} c_{im} m_m$$

Generalizing this result to j=1...p provides the solution shown in section II-1.

APPENDIX B

The most frequently occurring morning inversion height, H, between the years 1950 and 1974 was 350 meters (AQMD, 1980. The distance traveled by one vehicle was averaged at 10^4 miles/year. The gasoline-powered vehicle registration in 1971 was 4.2×10^4 vehicles, the gasoline consumed that year was averaged at 8.7×10^6 gals/day (APCD, 1971). Thus, the average gas mileage, G, was 13.2 miles/gal.

The lead content of Los Angeles gasoline, L, for the year 1972 was averaged at 0.56 g/L (Huntzicker et al., 1975). The mass fraction of airborne lead, α, per unit input estimated from Huntzicker et al., was 0.32.

The traffic density, d, at site 1 (see Table 9 in text) between June 1971 and June 1972 was 2×10^5 vehicles per square mile and per day while the lead mass concentration, ρ, was 5.35 $\mu g/m^3$ (Gordon and Brian, 1973).

Based on these results, an average residence time, θ, can be computed as follows:

$$\theta = 16.4 \frac{\rho x H}{(\alpha x L)(d/G)} \simeq 11 \text{ hours}$$

where 16.4 is a units conversion factor.

APPENDIX C

Table 12. Pattern of Refinery Contributions at Site 3

PAH	Sampling Period		Arithm.	PAH/BeP[a]
	June 71-June 72	Dec. 72-Dec. 73	Mean	
BFL	2.01	2.39	2.20	1.60
BaP	2.64	2.63	2.64	3.93
BeP	1.41	1.38	1.40	1.00
BghiP	2.90	1.82	2.36	2.03
ANTH	0.60	0.58	0.59	2.01
COR	0.33	-0.19	0.07	0.05

[a]All PAH were corrected for their decay.